

**Synthesis, Characterization, and Application of Gold  
Nanoparticles in Green Nanochemistry  
Dye-Sensitized Solar Cells**

**by Hailey E. Cramer, Mark H. Griep, and Shashi P. Karna**

**ARL-TR-6034**

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## **Synthesis, Characterization, and Application of Gold Nanoparticles in Green Nanochemistry Dye-Sensitized Solar Cells**

**Hailey E. Cramer**  
University of Delaware

**Mark H. Griep**  
National Research Council

**Shashi P. Karna**  
Weapons and Materials Research Directorate, ARL

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14. ABSTRACT Gold (Au) nanoparticles (NPs) have a wide range of scientific applications due to their innate ability to efficiently bind with organic and bio molecules in conjunction with possessing excellent optical properties. In this experiment, Au NPs were synthesized and experimentally characterized via atomic force microscopy, high-resolution tunneling electron microscopy, and ultraviolet-visible spectroscopy. After characterization, the NPs were found to vary in shape but had a uniform size of 25 nm, with an absorption maxima at 521 nm. Using their bio-binding properties and light absorption characteristics, the NPs were integrated with anthocyanin-based, dye-sensitized solar cells. The hybrid system was found to enhance the photovoltaic output of the system, likely due to the enhanced photon-capturing capacity provided by the Au NPs.					
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## 1. Introduction and Background

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Nanoparticles (NPs) range from 1 to 100 nm in diameter and can display atom-like discrete energy levels and a high surface-to-volume ratio. These excitons are quantum confined and thus change the NPs' properties and behavior drastically from the bulk material. Depending on size, NPs can have a broad absorption and fluoresce from the ultraviolet (UV) to the infrared. As NPs shrink in size, their emission wavelength gets smaller and they gain more energy. Since NP sizes can be tuned, scientists have been able to control their optical, electrical, magnetic, and chemical properties. For this reason, NPs have many applications in modern technology, specifically in light-emitting diodes, transistors, alternative energy, and biomedicine (1). The NPs can be engineered for specific applications based on their composition; due to their relatively limited number of atoms, interesting phenomena occur upon creation of excitons (2).

Chemical synthesis of NPs, which has been found to be easy and inexpensive, involves the creation of a colloidal suspension of a precursor, organic surfactant, and solvent. When the solution is heated, the precursors form into monomers. The solution becomes super saturated with formed monomers and begins to grow NPs. Through specific chemical solutions, the size of the NPs can be tuned for multiple applications. Gold (Au) NPs are specifically valued because of their intense fluorescence and ability to bind with organic materials.

Chemical synthesis of Au NPs involves the slow reduction of Au salts ( $\text{HAuCl}_4$  or  $\text{AuBr}_3$ ) into a solution. Volpe et al. (3) created Au quantum dots by reducing  $\text{HAuCl}_4$  into alcoholic solutions of polyvinylpyrrolidone and ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ). The quantum dots, characterized using a transmission electron microscope, were found to be an average size of 4.5 nm. Lee and Meisel (4) created Au NPs by mixing  $\text{HAuCl}_4$  with ice-cold  $\text{NaBH}_4$ . Polyvinyl alcohol was then added and the solution was boiled. This method was effective at creating NPs that adsorbed dyes. Zheng et al. (5) were able to create highly fluorescent, water-soluble, size-tunable Au NPs by reducing  $\text{HAuCl}_4$  into aqueous poly(amidoamine) dendrimers. The NPs were found to have discrete absorption and fluorescence from the UV spectrum to near infrared. Bauer et al. (6) and McFarland et al. (7) were also able to change the size of the NP clusters through a sodium citrate reduction method involving  $\text{HAuCl}_4$ . Bauer et al. (6) were able to control the size of the clusters by varying the amount of sodium citrate added to solution. In this work, we utilized the citrate reduction approach (6, 7).

Nanoparticles have also been studied for photovoltaic applications and, specifically, dye-sensitized solar cells (DSSCs). DSSCs have caught recent attention as a potential alternative to silicon solar cells due to their low cost, ease of manufacturing, tenability, and robustness /flexibility (8). They are not inherently brittle, as with silicon-based technologies, and do not have to be positioned at a specific angle of incidence. They can also be engineered to be flexible, which would allow them to be sold by the roll. Using nanoparticles to enhance

photovoltaic efficiency of DSSCs was introduced by Oregan and Gratzel in 1991 (9). The titania nanostructures create a porous surface, which yields an abundance of surface area and allows light-harvesting dyes to be easily absorbed. When light is shined on the transparent electrode of the DSSC, the electrons in the highest occupied molecular orbitals in the dye molecules are excited to the unoccupied molecular orbitals, eventually move to the close-lying state of  $\text{TiO}_2$  nanoparticles, and are transported to the electrode. An  $\text{I}^-/\text{I}_3^-$  is used as a redox couple to replenish electrons to the dye molecules, thus creating a circuit. The photon-to-electron conversion process is more extensive compared to silicon solar cells. The dyes and electrolyte solution degrade over time, making DSSCs less efficient than silicon solar cells. However, the disadvantages of DSSCs are continually being addressed, allowing DSSCs to reach their potential as a cost-efficient alternative to silicon-based solar cells.

When Au NPs are synthesized to a preferred size and combined with other sized NPs, they can absorb many wavelengths. By combining multiple-sized NPs, wavelengths of light from the visible to infrared spectrum can be absorbed; if used in a DSSC, the DSSC could absorb more light and thus be more efficient. In this experiment, we synthesized Au NPs using a chemical synthesis procedure and combined them with anthocyanin dyes extracted from blackberries for DSSC systems.

Anthocyanin dyes have been of recent interest to nanobio research because of their ability to absorb light and convert it into electrons in a natural and inexpensive way (8). Anthocyanin is a highly conjugated ring molecule facilitating the movement of electrons through its structure. It belongs to the class of flavonoids and is found commonly in tissues of many different fruits and plants. In cell vacuoles, anthocyanin absorbs light in the blue-green region between the 450- and 600-nm wavelengths, which allows many fruits and plants to reflect red, purple, or blue. Depending on the type of anthocyanin, pH, the sugar attached, and where the sugar is located on the anthocyanin molecule structure, the anthocyanin will absorb different ultraviolet-visible (UV-Vis) wavelengths. Anthocyanin dyes are also powerful antioxidants and have many health benefits, including removal of toxic-free radicals from the body. Anthocyanin dyes have also been shown to function well in DSSC systems.

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## 2. Materials and Methods

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The DSSCs used in this experiment were composed of a fluorine-doped, tin-oxide (FTO)-coated glass substrate which was coated with a thin layer of  $\text{TiO}_2$  nanoparticles to which anthocyanin dye had been absorbed. A platinum-coated glass plate was used as a counter electrode, and an iodide/triiodide ( $\text{I}^-/\text{I}_3^-$ ) electrolyte solution was placed between the plates.

## 2.1 TiO<sub>2</sub> Nanoparticle Substrate Preparation

To create a uniform TiO<sub>2</sub> nanoparticle solution to be deposited onto the glass substrate, 1.05 g of titanium dioxide nanopowder (Sigma Aldrich, <25 nm 99.7% metal basis) was slowly combined with 3.25 mL of 5% dilute acetic acid using a ceramic stirrer.

The TiO<sub>2</sub> solution was deposited using the doctor blading method in which the conductive sides of 2.54- × 2.54-cm FTO glass substrates were taped with Scotch\* tape about 5 mm from the edge on all four sides. The doctor blading method created a 40–50-μm trough in which the TiO<sub>2</sub> solution was spread using a glass slide to create a thin uniform layer. The Scotch tape was then removed, and the TiO<sub>2</sub> substrates were allowed to air dry for 10 min. The substrates were then annealed at 450 °C for 30 min, with a ramp speed of 20 °C/min to achieve anatase crystal phase (6).

## 2.2 Blackberry Anthocyanin Extraction Procedure

Blackberry anthocyanin was extracted through a mechanical extraction method in which blackberries were crushed to expose natural dyes using a mortar and pestle. This extraction method produced a slurry mixture containing anthocyanin molecules.

## 2.3 Au Nanoparticle Synthesis

Au NPs were synthesized through multiple colloidal synthesis procedures involving varying amounts of the reducing agent trisodium citrate in order to determine if the amount of trisodium citrate added affected the size of the Au NPs. This included adding 2, 5, and 20 mL of trisodium citrate. During the 2-mL trisodium citrate procedure, 10-mg tetrachloroauric [III] acid trihydrate (HAuCl<sub>4</sub> · 3H<sub>2</sub>O) in 100 mL of water was heated to boiling. Once at a boil, 2 mL of 1% (w/v) trisodium citrate dehydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> · 2H<sub>2</sub>O) were added and stirred constantly. An obvious change of color from yellow to dark red occurred after about 15 min. At this point, the solution was removed from the heat and placed into an ice bath. The same procedure was applied for the 5- and 20-mL trisodium citrate solutions. Once the Au salt solution reached the boiling point, the 5- and 20-mL solutions were each added and removed from the heat after 15 min. During the 20-mL sodium citrate procedure, 4 mL of solution was extracted at 9, 12, 14, and 28 min to determine if timing affected NP size as well.

Experimental characterization of the particles was used to determine the quantum dot morphology and optical properties. This was performed using UV-Vis, fluorescence spectroscopy, and high-resolution tunneling electron microscopy (HR-TEM).

## 2.4 DSSC Assembly

Annealed TiO<sub>2</sub> nanoparticle photoanodes were placed into 10 mL each of the blackberry anthocyanin dye and allowed to absorb into the TiO<sub>2</sub> surface for 3 h. After 3 h, each photoanode

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\* Scotch tape is a registered trademark of 3M Company.

was washed with ethanol to remove excess anthocyanin and other particulates. Petri dishes containing 2, 4, and 6 mL of the 5-mL sodium citrate Au NPs were created, and one photoanode with absorbed anthocyanin was placed into each. Au NPs were allowed to absorb for 3 h. After absorption, each photoanode was washed with ethanol to remove excess NPs, and the sample was dried with nitrogen. Each photoanode was then placed face down onto the conductive side of a platinum-coated counter electrode. The plates were sealed together with two binder clips, and 15  $\mu$ L of an  $I^-/I_3^-$  electrolyte solution was pipetted between the electrodes to coat the entire  $TiO_2$  surface. The platinum counter electrodes were created by sputtering platinum onto FTO-coated glass substrates to create a platinum thin film of about 50 nm. The  $I^-/I_3^-$  was prepared by mixing 3.346 g LiI, 634.522 mg  $I_2$ , and 4.056 g 4-tert-butylpyridine in 50-mL acetonitrile. A deconstructed DSSC (before sealing platinum counter electrode and photoanode together) and a completed DSSC ready for testing can be seen in figures 1a and b, respectively.

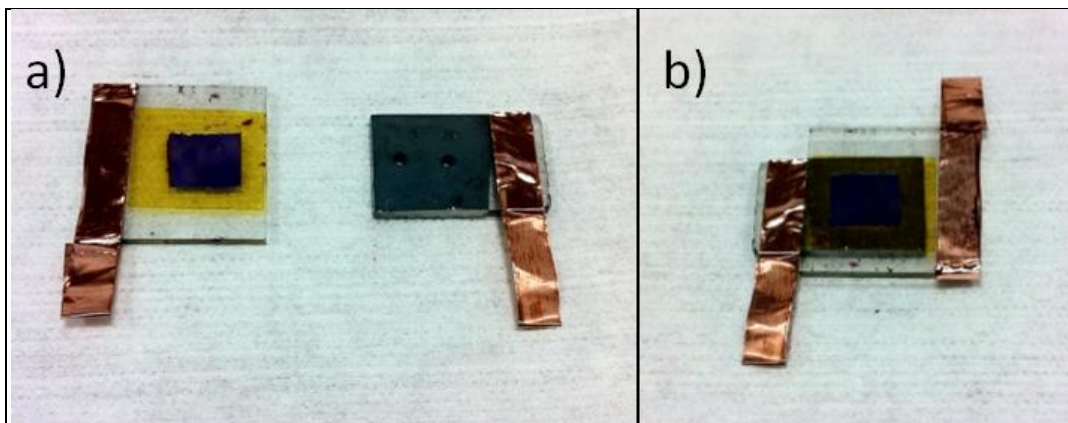


Figure 1. (a) DSSC photoanode and platinum counter electrode and (b) completed DSSC.

## 2.5 DSSC Photovoltaic Measurement

Current-voltage (I-V) measurements were taken on and analyzed with a Keithley 6430 semiconductor analyzer unit and LabVIEW program. A piece of electrical tape to which a  $0.5 \times 0.5$ -cm square had been cut out was placed onto the DSSC to expose only a  $0.25 \text{ cm}^2$  area to allow consistent testing between samples. During testing, a 100-W Xenon light source was set to 100 mW and shined on the DSSC in ambient lighting. The overall efficiency ( $\eta$ ) of the DSSC was calculated from the integral photocurrent density ( $i_{ph}$ ), the open-circuit voltage ( $V_{oc}$ ), the fill factor (FF), and the intensity of the incident light ( $I_s$ ), as shown in equation 1.

$$\eta = \frac{i_{ph} \times V_{oc} \times FF}{I_s}. \quad (1)$$

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### 3. Results and Discussion

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#### 3.1 Au NP Characterization

Samples of the 20-mL sodium citrate Au NP solution were taken at different points in the synthesis procedure (9, 12, 14, and 28 min). As shown in figures 2a and b, a difference in color could be observed at each stage. Multiple characterization techniques were used to determine if the change in color related to NP particle size and also to determine if the amount of reducing agent affected size.

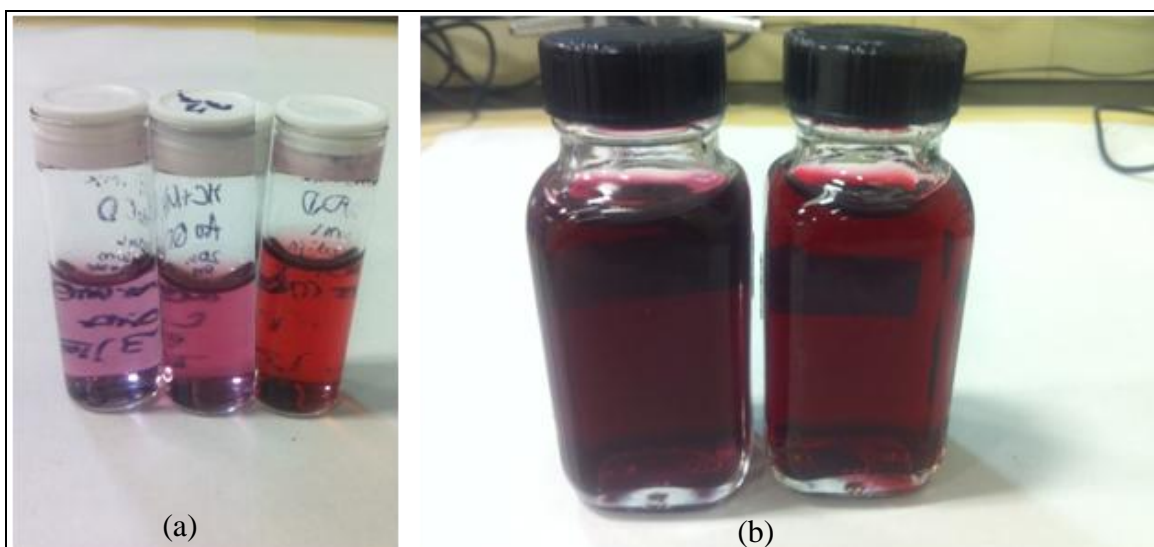


Figure 2. (a) Color changes of Au NP solution at 9, 12, and 14 min, respectively, and (b) color of solution after 28 min of boiling.

Optical properties of the four samples were characterized using a Photonics charge-coupled diode array UV-Vis spectrophotometer and a Horiba FluoroMax-3 fluorescence spectrometer. As shown in figures 3a and b, the 2- and 5-mL trisodium citrate solutions were found to have absorbance peaks at 521 nm. This was also true in all 20-mL sodium citrate solutions, as shown in figure 4.

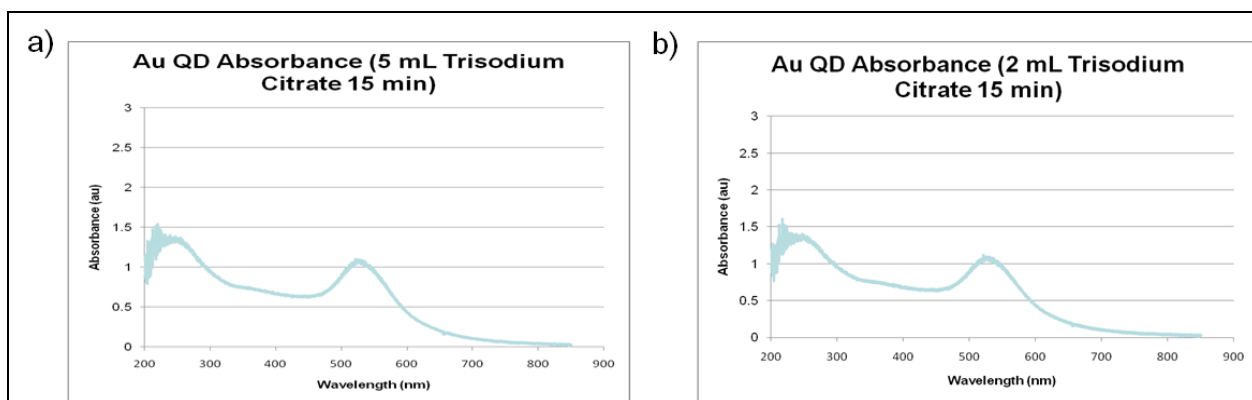


Figure 3. UV-Vis absorbance spectrum of (a) Au NP 5-mL sodium citrate and (b) 2-mL sodium citrate.

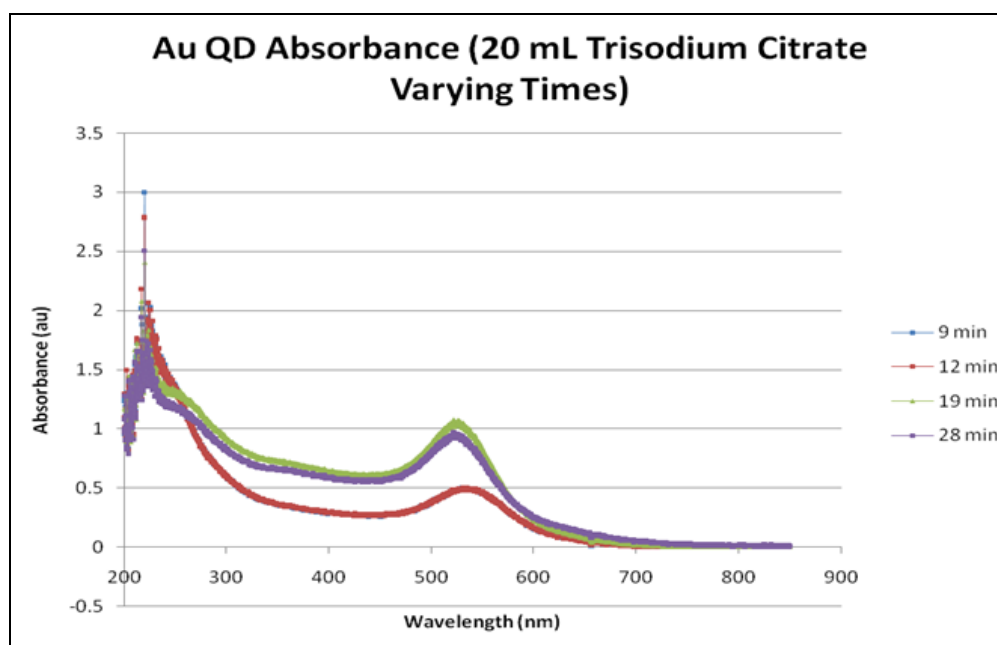


Figure 4. UV-Vis absorbance spectrum of Au NP 20-mL sodium citrate solution after 9-, 12-, 19-, and 28-min boiling times.

To determine the size of the Au NPs, atomic force microscopy (AFM) and HR-TEM were performed. Figure 5 shows AFM photos of Au NPs from each of the trisodium citrate reductions. AFM images of the 2-mL trisodium citrate solution are shown in figures 6a and b and were found to produce Au NP clusters about 15 nm high and 200 nm wide. In figures 6c and d, similar-sized Au NP clusters can be observed for the 20-mL trisodium citrate solution at 28 min.

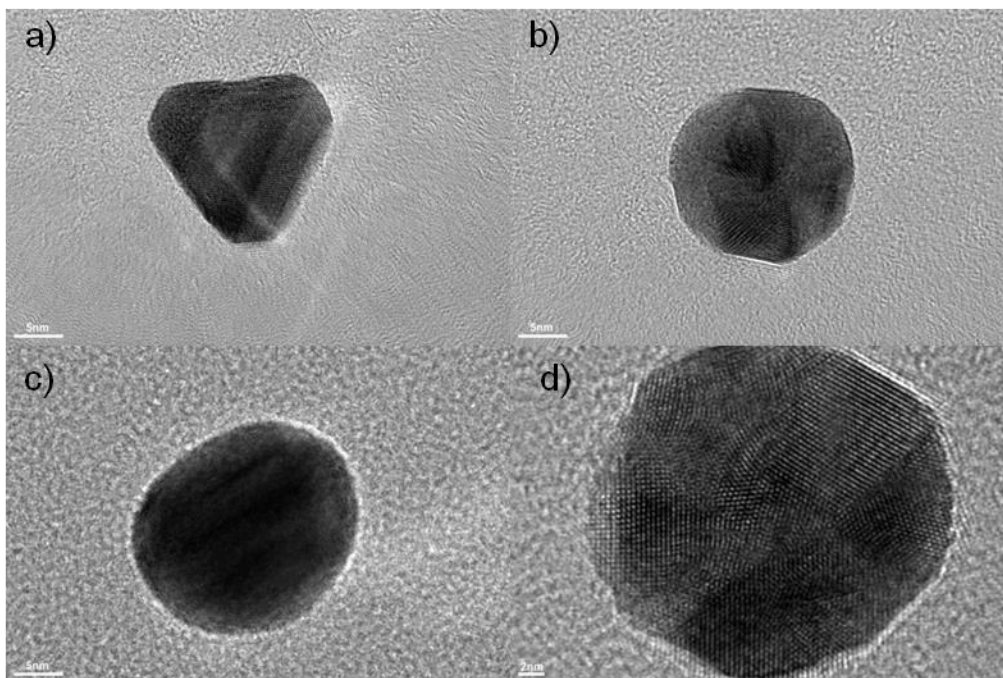


Figure 5. HR-TEM image of Au NP 5-mL sodium citrate, with size of ~25 nm.

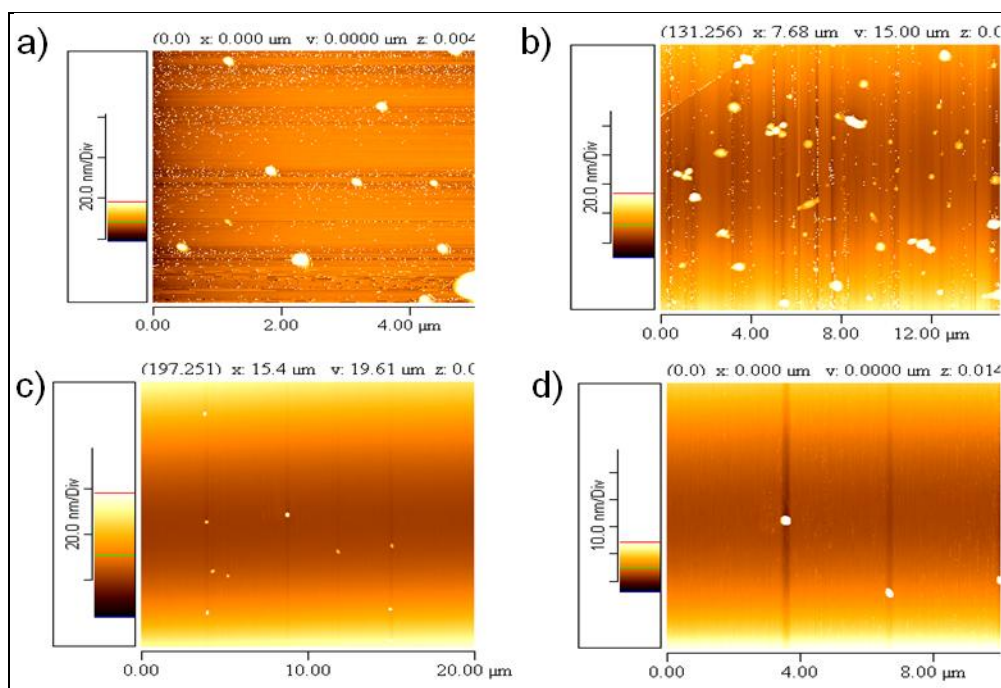


Figure 6. Noncontact mode AFM image of (a and b) Au NPs 2-mL sodium citrate and (c and d) Au NPs 20-mL sodium citrate after 28 min of boiling (Au NPs in 15-nm-diameter clusters).



Through HR-TEM, figure 5 shows that the 5-mL trisodium citrate solution, which had been sonicated to break up clusters, contained varying shaped Au QDs with strong crystalline structures measuring around 25 nm in diameter.

### 3.2 Au NPs in DSSCs

Functional DSSCs were created utilizing Au NPs from the 20-mL sodium citrate (28-min boiling) method. The photoanode topology was analyzed by AFM to reveal a porous structure, with an average roughness <200 nm, as shown in figure 7a. A scanning electron microscopic (SEM) image, shown in figure 7b, confirmed a continuous TiO<sub>2</sub> nanoparticle film of about 15- $\mu$ m thickness.

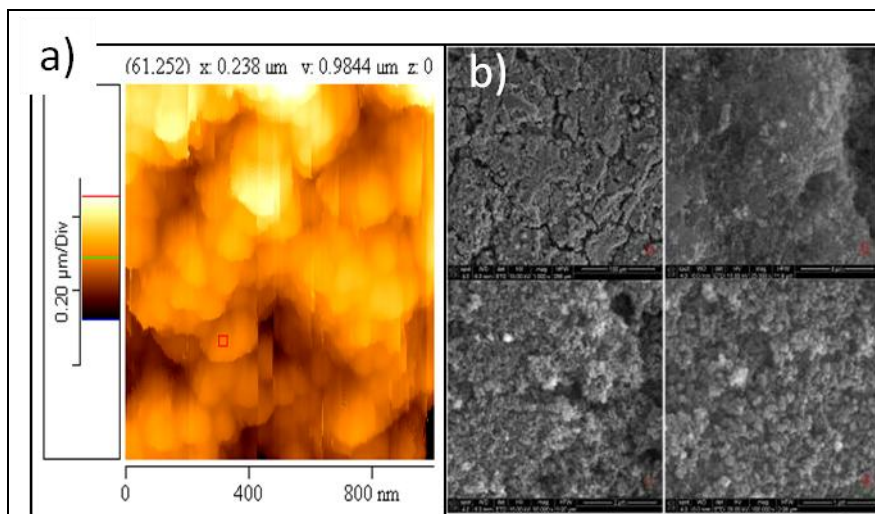


Figure 7. (a) AFM image of TiO<sub>2</sub> surface and (b) SEM image of TiO<sub>2</sub> surface.

Electrical I-V measurements of the DSSCs were measured with a Keithley semiconductor analyzer using a 100-mW/cm<sup>2</sup> input power. Figure 8 shows the measured I-V curves of the DSSCs after blackberry anthocyanin absorption and the absorption of 2, 4, and 6 mL of Au NPs. It also gives the I-V curves of the Au NP and anthocyanin controls. Calculated values of the purified DSSCs can be seen in table 1.

From the I-V trace in figure 8 and the photocurrent density values listed in table 1, it can be seen that a substantial increase in photocurrent output is achieved by adding Au NPs to the anthocyanin sensitized solar cell. From the absence of usable output achieved with Au NPs alone, adding Au NPs hybridized on top of the anthocyanin steadily increased photocurrent output by 5.4%, 13.8%, and 29.6% for cells soaked in 2-, 4-, and 6-mL Au NP solutions, respectively. Since the Au NP solutions had the same concentration, the data suggests that heavy NP loading occurred and that the lower volumes didn't achieve full NP loading. The data also displays a continuing increase in photocurrent enhancement, suggesting that the maximum Au NP loading had not yet been reached.



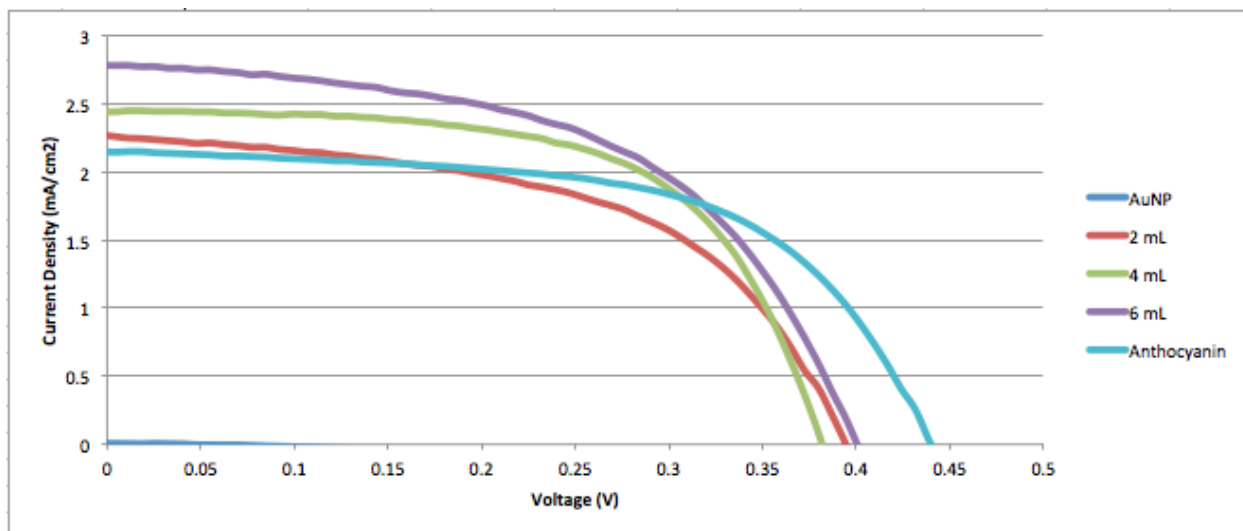


Figure 8. Gold nanoparticle current enhancement blackberry anthocyanin dye DSSCs.

Table 1. DSSC efficiency values and calculations.

Dye	Efficiency (%)	Fill Factor (%)	Photocurrent Density (mA/cm <sup>2</sup> )	Open Circuit Voltage (mV)
Anthocyanin	0.56	59.6	2.144	439
Au NP	$5.8 \times 10^{-5}$	20.8	0.0069876	40.2
Au NP-2 mL	0.47	54.0	2.26	387
Au NP-4 mL	0.56	60.5	2.44	379
Au NP-6 mL	0.59	54.0	2.78	394

In contrast to the increasing photocurrent, the open circuit photovoltage was reduced due to the addition of Au NPs. Based on Au NP loading, no apparent correlation is seen to distinguish this phenomena. This decrease in photovoltage could likely be from increased resistance within the cell and more obstacles for the electrolyte to pass in order to recharge the anthocyanin molecule. With the open circuit photovoltage decreased on average by 11.9%, the resulting cell only showed minimal increases in overall photoconversion efficiencies.

## 4. Summary and Conclusions

Varying shaped Au NPs, with an average size of 25 nm, were successfully synthesized and characterized through this experiment. It was found that there was no significant difference in size between varying sodium citrate amounts or boiling times. When used in TiO<sub>2</sub> DSSCs and combined with blackberry anthocyanin dye, Au NPs in 4 and 6 mL were found to produce more current than a DSSC fabricated only with the blackberry anthocyanin dye. Although this was only a slight increase in current output, only one size of Au NPs was used and absorbed at one

wavelength (521 nm). If paired with other sizes of NPs, the solar cell could be made more efficient by absorbing more of the visible spectrum. This experiment could be explored in the future with other NP compositions. Anthocyanin dye and Au NPs could also be allowed to absorb into the TiO<sub>2</sub> DSSCs for longer periods of time and at higher concentrations to allow maximal NP loading.

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## List of Symbols, Abbreviations, and Acronyms

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AFM	atomic force microscopy
Au	gold
DSSC	dye-sensitized solar cell
FTO	fluorine-doped, tin-oxide
HR-TEM	high-resolution tunneling electron microscopy
I-V	current-voltage
NPs	nanoparticles
SEM	scanning electron microscopic
UV	ultraviolet
Vis	visible

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